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INFRARED SPECTRA OF URANYL PHOSPHATE, OXALATE, AND SALICYLATE IN THE SOLID STATE

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ABSTRACT. The infrared spectra of three compounds, uranyl phosphate, uranyl oxalate, and uranyl salicylate have been studied in the region $2-24\mu$ using potassium bromide disc and nujol mull methods. About 35 bands in the case of phosphate, 25 in the case of oxalate and 40 in the case of salicylate are obtained from both these methods. The vibrational frequencies obtained from the infra-red work are correlated with those obtained form flourescence experiments.

INTRODUCTION

Corn and Wu (1938) are the first to study the infra-red and Raman spectra of uranyl acetate, nitrate, chloride and sulphate and establish the frequencies 860, 210, and 930 cm^{-1} characterising the uranyl ion. The infra-red spectra of a number of simple and double uranyl salts were studied later by Lecomte and Freymann (1941) who confirmed the above frequencies. Sevchenko and Stepanov (1949) studied the spectra of the uranyl acetate, nitrate, sulphate and potassium sulphate in the region of overtones of the above frequencies and came to the conclusion that the uranyl ion is linear in the case of acetate and nitrate and bent in the case of sulphate and potassium sulphate. All the above workers confined their investigations to the NaCl prism region only i.e., up to 15 μ.

In the present investigation, the infra-red spectra of three compounds, uranyl phosphate ($HUO_2PO_4 . 4H_2O$), uranyl oxalate [$UO_2(COOH)_2\ 3H_2O$] and uranyl salicylate, $UO_2[C_6H_4(OH)COO]_2$ have been studied in the region $2-24\ \mu$. The phosphate has been studied for the first time. The oxalate and salicylate were also studied by Lecomte and Freymann who, however, obtained bands, only in the region 800-1600 cm^{-1}. Even in this region, the positions of the absorption bands have been indicated in a table but the actual values of the frequencies were not given.

EXPERIMENTAL TECHNIQUE

The infra red spectra are recorded using two different methods : (1) potassium bromide disc method and (2) nujol mull method. In the case of KBr disc method

(Ford and Wilkinson, 1954), a Hilger automatic double beam prism spectrometer has been used with a rock salt prism for the region 2-15 μ. The wavelength scale is linearly calibrated in microns and the dispersion is 4.5 cm per micron. Calibration marks are made on the recorder chart, at regular intervals by a small and rapid deflection of the pen. A mixture of between 0.1 and 1.0 per cent of the sample and chemically pure potassium bromide is grinded into a fine powder and then pressed under vacuum to produce clear and transparent disc The advantage of this method is a better distribution of very small particles in the suspending medium and the elimination of the obscuring bands which occur with mulling agents.

In the case of nujol mull method, spectra are recorded on a single beam Perkin Elmer infrared spectrometer (Model 122) with substances suspended in the nujol mull, in the region 2—24μ using the sodium chloride and potassium bromide prisms. To obtain the absorption only due to substance, the transmission curve of the nujol is also recorded on the same record chart with the same experimental conditions. After substracting the absorption due to nujol, the transmission coefficients have been calculated for each point and a graph is drawn between the percentage transmission and wavenumbers.

RESULTS

A comparison of the frequencies of bands obtained from the potassium bromide disc and nujol mull methods, shows that there is reasonable agreement between the two data. However, the absorption bands with the potassium bromide disc method are sharper and better resolved than in the case of nujol mull method

The frequency values of the bands are given in Tables I, II and III and the curves are given in Figs. (1 to 9) The UO_2^{++} ion fundamentals are recorded in all cases. A few bands could be also combination bands. The large number of other bands may consist of combinations of υ_1, υ_2 and υ_3 of UO_2^{++} ion or fundamentals, combinations and overtones of other radicals of the salts. Prominent examples are the bands due to water of hydration in the 3400-3500 cm^{-1} region and the C = 0 frequencies in oxalate and salicylate occurring in the region 1600-1700 cm^{-1}.

The fluorescence and absorption spectra of these compounds are also studied by the author at liquid air temperature with powder samples (Details of these results will be published elsewhere) It is found that the phosphate and oxalate are fluorescent and the salicylate has not shown any fluorescence at all. The ground state frequencies obtained from the analyses of the fluorescence spectra are given in the third column of Table I, II, and III for correlation of the results. It is seen that there is good agreement between the various data.

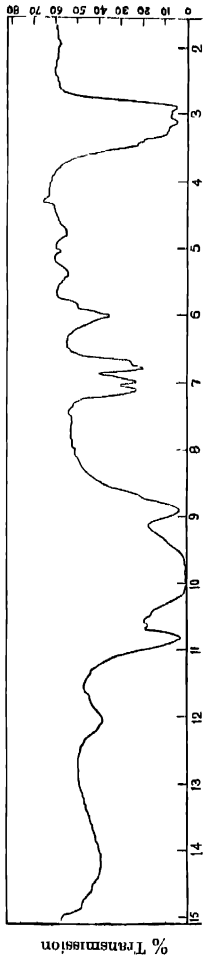

Fig. 1. Infrared absorption spectrum of uranyl phosphate (KBr disc method)

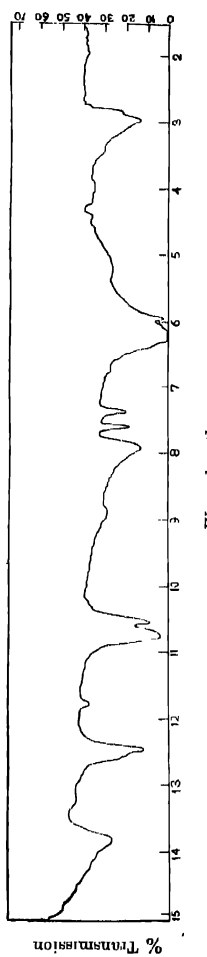

Fig. 2. Infrared absorption spectrum of uranyl oxalate (KBr disc method)

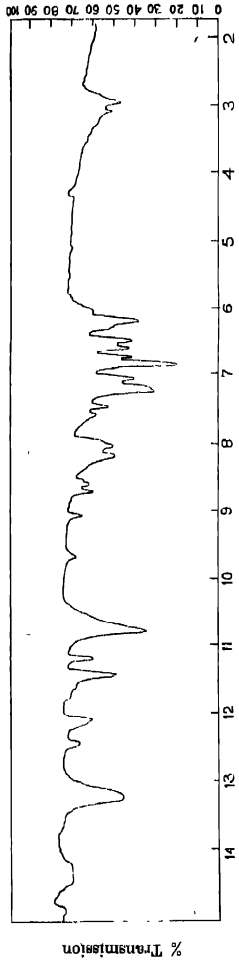

Fig. 3. Infrared absorption spectrum of uranyl salicylate (KBr disc method)

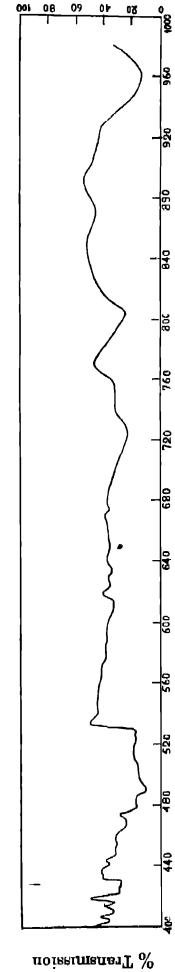

Fig. 4. Infrared absorption spectrum of uranyl phosphate (Nujol mull method.)

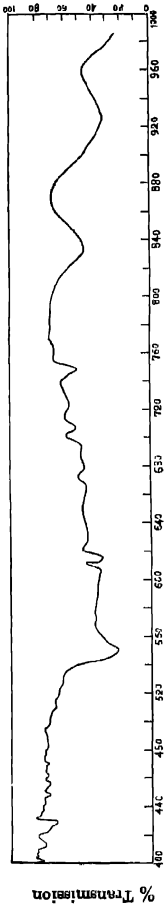

Fig. 5. Infra-red absorption spectrum of uranyl oxalate (Nujol mull method.)

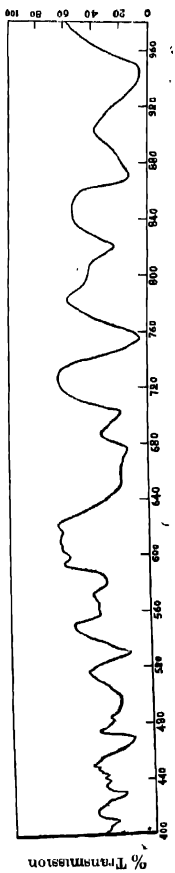

Fig. 6. Infrared absorption spectrum of uranyl salicylate (Nujol mull method)

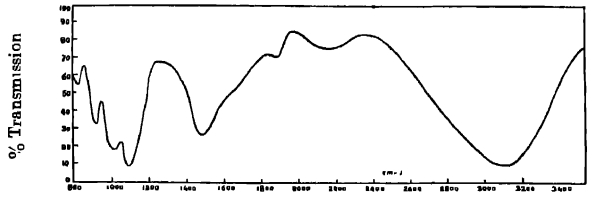

Fig 7. Infrared absorption spectrum of uranyl phosphate (Nujol mull method)

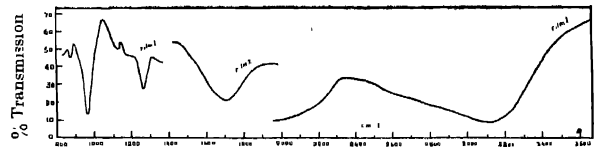

Fig. 8. Infrared absorption spectrum of uranyl oxalate (Nujol mull method)

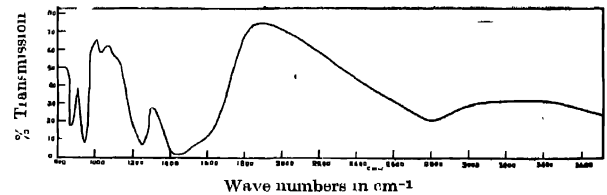

Fig. 9. Infrared absorption spectrum of uranyl salicylate (Nujol mull method)

TABLE I

Infrared absorption bands of uranyl phosphate

Wavenumber of the band in cm^{-1}			
Potassium bromide disc method	Nujol mull method	Fluorescence	Remarks
1	2	3	4
	550 (vs)		
	607 (w)		
	615 (m)		
	666 (w)		
671 (w)	680 (w)		
704 (m)	707 (m)		
	723 (w)		
	749 (s)		
818 (w)			
828 (m)	834 (s)	828	ν_1 fundamental
852 (w)			
877 (w)			
921 (vs)	926 (vs)	909	ν_3 fundamental
938 (w)			
954 (w)			
1011 (vs)	1020 (s)		182 + 828 = 1010
1119 (vs)	1110 (vs)		182 + 921 = 1103
1359 (w)			
1401 (s)			
1429 (s)			
1468 (s)			
1484 (m)	1500 (vs)		
1656 (s)			$2 \times 828 = 1656$
1712 (w)			
1848 (m)			$2 \times 921 = 1842$
	1900 (m)		
1972 (w)			
2079 (m)			
	2180 (m)		
2278 (w)			
2841 (w)			
2985 (w)			
3067 (w)			
3155 (vs)	3130 (vs)		Water of hydration
3425 (vs)			Water of hydration

w—weak; m—medium; s—strong; vs—very strong; b—broad.

TABLE II

Infrared absorption bands of uranyl oxalate

Wavenumber of the band in cm^{-1}			
Potassium bromide disc method	Nujol mull method	Fluorescence	Remarks
1	2	3	4
		257	ν_2 fundamental
	625 (w)	609	Oxalate frequency
	635 (w)		
672 (w)	675 (w)		
710 (w)			
723 (s)	725 (m)		
755 (w)			$3 \times 257 = 771$
796 (w)			
803 (s)	806 (s)		
849 (w)	870 (m)	875	ν_1 fundamental
928 (vs)			
947 (s)	961 (vs)	961	$\nu_3$fundamental
1123 (w)	1130 (w)		$849 + 257 = 1106$
1259 (s)	1250 (s)		
1316 (m)			
1355 (m)			$849 + 2 \times 257 = 136$
1383 (w)			
1473 (w)			
1606 (s)			
1629 (vs)		1672	C = O frequency
1686 (s)	1700 (s)		
1920 (m)	1950 (w)		$2 \times 947 = 1894$
2907 (w)			
	3210 (s)		
3378 (s)			Water of hydration
3546 (w)			

TABLE III

Infrared absorption bands of uranyl salicylate

Wavenumber of the band in cm^{-1}		
Potassium bromide disc method	Nujol mull method	Remarks
	530 (s)	
	557 (w)	
	580 (s)	
	597 (w)	
	616 (w)	
	652 (w)	

TABLE III (*contd.*)

Infrared absorption bands of uranyl salicylate

Wavenumber of the band in cm^{-1}		
Potassium bromide disc method	Nujol mull method	Remarks
1	2	3
669 (w)	675 (m)	
695 (b)	700 (s)	
756 (vs)	755 (vs)	
803 (m)		
827 (m)	819 (s)	
848 (w)		
859 (w)		
875 (m)	870 (s)	ν_1 fundamental
892 (m)		
929 (vs)	945 (vs)	ν_1 fundamental
1033 (w)	1035 (w)	
1101 (m)		
1147 (m)		
1160 (w)		
1219 (m)		
1242 (m)	1250 (vs)	
1309 (w)		
1319 (w)		
1340 (m)		
1385 (vs)		
1393 (w)		
1420 (m)	1440 (vs)	
1466 (vs)		
1488 (m)		
1517 (m)		
1546 (m)		
1597 (w)		
1616 (s)	1600 (m)	C=O frequency
1653 (w)		
1805 (w)		
1949 (w)		
	2800 (s)	
3215 (m)		Water of hydration
3367 (s)		

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